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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Reaction studies of elemental fluorine with organic molecules has lead to an understanding of mechanisms of the addition of molecular fluorine to unsaturated carbon-carbon bonds. The sensi- tivity of the activation energy of molecular fluorine to various molecular properties has been explored through extensive studies of closely related hydrocarbons. The effect of heteroatoms in a variety of hydrocarbons has also been explored. (over)		

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cont The studies of molecular fluorine reactions with inorganic fluorides has led to the identification of many new unstable fluorine species such as UF_5 , MUF_x where M is an alkali atom and x varies from four to seven. Studies of the interaction of inorganic fluoride species has provided insight into the Lewis base character of transition and main group metal fluorides.

The study of interactions and reactions of metal atoms with small Lewis bases has provided an understanding of the important intermediate steps in the reductive chemistry of water and methane with various metals.

Novel experimental approaches to the preparation of new metal oxyfluorides and nitrifluoride are also described.

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⑥ INORGANIC SYNTHESIS AT HIGH TEMPERATURES
AND HIGH PRESSURES WITH SPECIAL INTEREST
IN THE PREPARATION OF NEW FLUORINE COMPOUNDS.

⑨ FINAL REPORT.

⑩ JOHN L. MARGRAVE

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FINAL REPORT

Research under sponsorship of U.S. Army Research Office during the past years has been concentrated in the area of fluorine chemistry. The following major topics have been investigated:

(1) Reactions of Organic Molecules with Elemental Fluorine

Temperatures

- (a) methane, ethane, and saturated hydrocarbons
- (b) ethylene, acetylene, and other unsaturated hydrocarbons
- (c) organic compounds containing oxygen and sulfur

(2) Reactions of Inorganic Fluorides at Low Temperatures

- (a) adducts of UF_4 and UF_6 with alkali and alkaline earth fluorides
- (b) reaction of lithium atoms with SiF_4
- (c) interaction of CO with metal fluorides
- (d) chlorination and bromination of UF_4
- (e) reaction of Sn and SnF_2 with C_2H_4

(3) Reactions of Metal Atoms with Lewis Bases

- (a) metal atoms + water
- (b) metal atoms + methane

(4) Synthesis of Metal Oxyfluorides

(5) Synthesis of Metal Nitrifluorides, and

(6) Further Studies of CFX.

(1) Reactions of Organic Molecules with Elemental Fluorine
Temperatures

(a) methane, ethane, and saturated hydrocarbons

When saturated hydrocarbons are co-deposited with elemental fluorine in matrices at liquid helium temperatures there is no spontaneous reaction. The saturated hydrocarbons are distributed throughout the fluorine matrix and, rather interestingly, the F_2 molecule is one of the least perturbing matrix molecules we have observed. The infrared absorption spectra of matrix isolated methane, ethane, etc. are very close to the gas phase spectra. The matrix perturbation effects are very slight, of the order of $1-5\text{cm}^{-1}$ and at 12K the spectra are exceedingly sharp and well defined. Though no reaction occurs between F_2 molecules and saturated hydrocarbons one can induce reaction by uv photolysis which dissociates the F_2 and provides fluorine atoms which are exceedingly reactive. One finds mono, di, tri, and tetrafluoromethanes and higher fluorinated species, of course, for the higher members of the alkanes.

(b) ethylene, acetylene, and other unsaturated hydrocarbons

Reactions of molecular fluorine with unsaturated hydrocarbons were studied in fluorine and argon fluorine matrices. Certain hydrocarbons (acetylene, benzene, etc.) could be condensed into a pure fluorine matrix without reaction. Ethylene and allene could also be condensed in fluorine without reaction, but did

react when exposed to light in the wavelength region from 1 to 4 μ . The ethylene reaction produced either 1,2-gauche- and trans-difluoroethane or vinyl fluoride and hydrogen fluoride. Propylene, butadiene, and cyclohexene reacted (spontaneously) with molecular fluorine in low-temperature matrices.

Only the alkenes with the highest ionization potentials can be trapped in a fluorine matrix without reaction. Sensitive EPR measurements have also suggested that some reaction of ethylene with fluorine does occur during the trapping process. The other alkenes apparently require very little activation energy for reaction with molecular fluorine since the reactions are occurring on a cold matrix surface. One might correlate this increased reactivity with their lower ionization potentials; however, the lack of reaction by cyclopropane and benzene indicates that a lower ionization potential is not the only factor involved in predicting the likelihood of spontaneous reaction with molecular fluorine at low temperatures. The ability of alkenes to form stable charge-transfer complexes with halogens probably contributes significantly to their increased reactivity.

The nature of the absorption which leads to photolysis of the complex is uncertain. Possibilities include excitation of a perturbed fluorine molecule or perhaps an overtone of the perturbed ethylene. The large deuterium isotope effect on the reaction rate suggests that excitation of carbon hydrogen vibrational modes plays a major role in the transition.

The increased yield of vinyl fluoride in the dilute F_2/Ar matrices can be explained in a number of ways. If the reaction is visualized as proceeding through a hot 1,2-difluoroethane intermediate, one can explain the different amounts of vinyl fluoride formed as due to the different quenching rates for pure fluorine and fluorine argon matrices. A pure fluorine matrix should be a better quencher because of the presence of an F_2 internal vibration. The increased quenching rate would decrease the probability of hot 1,2-difluoroethane decomposing into vinyl fluoride. The presence of both gauche and trans forms when the ethylene- F_2 adduct is quenched from the hot state is consistent with previous studies in which 1,2-difluoroethane was heated prior to trapping in an argon matrix.

The effect of quenching would be the same if the reaction proceeded with the first fluorine undergoing addition to the double bond producing a hot 1-fluoroethyl radical in the presence of the second fluorine atom. Radical recombination to form the difluoroethane would have no activation energy whereas fluorine atom attack on a carbon hydrogen bond would require some activation energy. Thus, rapid quenching would lead to increased 1,2-difluoroethane formation.

Either of the above mechanisms requires a difference in quenching rates for the fluorine and argon fluorine matrices. An alternate explanation could be based on a F_2 concentration effect where a 1:1 ($F_2-C_2H_4$) adduct reacts to form vinyl fluoride

while a 2:1 ($F_2-C_2H_4-F_2$) adduct reacts to form difluoroethane. This seems less likely since the relative amounts of vinyl fluoride and difluoroethane remained approximately the same when the F_2/Ar ratio was changed.

The implications of the work discussed here, which were first made known at the Washington meeting of the American Chemical Society, September, 1979, formed the basis for a laser photolysis study of the ethylene-fluorine matrix in the laboratory of Professor George Pimentel at Berkeley. We were in close contact with Dr. Pimentel as he followed up our first observation of this phenomenon with a laser irradiation experiment whereby he was able to excite selected ethylene vibrations with an infrared laser system. Exactly as our work had predicted, the region around $2,000-3,000\text{cm}^{-1}$ was exceedingly sensitive and when the laser radiation was matched to the ethylene absorption, direct fluorination did occur. Our original observations and the followup laser experiment by Pimentel and associates represents one of the clearest demonstrations of how selective photolysis may perhaps find practical application in industrial chemistry.

(c) organic compounds containing oxygen and sulfur

Preliminary experiments with organic molecules containing oxygen (CO , CO_2 , C_3O_2 , COS , CS_2 , $(CH_3)_2SO$, etc.) are in progress. The reaction products are still only partially characterized

but it appears clear that a variety of interesting COF, CSF, CF and SF species can be prepared by this method. The identification of complex molecules from infrared spectra alone is speculative but Table I summarizes the reactions and reaction products which we believe we have observed. Further studies are in progress.

(2) Reactions of Inorganic Fluorides at Low Temperatures

(a) adducts of UF_4 and UF_6 with alkali and alkaline earth fluorides

The present work has been carried out in an attempt to obtain i.r. spectra of a series of uranium fluoride anions, $[UF_4]^-$, $[UF_5]^-$, $[UF_6]^-$ and $[UF_7]^-$. These species are present in various macroscopically available salts which are not expected to be easily volatilized. Gas-phase spectra are therefore not available. However, dilute, frozen, argon matrices containing these anions should provide a reasonable model of the gaseous state. The anions can be generated in the matrix by reaction of the uranium fluorides with either alkali metals or alkali metal fluorides in argon at cryogenic temperatures to form MUF_4 , MUF_5 , MUF_6 , M_2UF_8 and MUF_7 species.

It can be seen from the data in Table II that the reduction of each of the uranium fluorides caused a shift to lower frequencies, i.e., a decrease of the force constant. This effect has been discussed in terms of the ionic character of the U-F

TABLE I
MOLECULES TRAPPED IN A PURE FLUORINE MATRIX AT 15K

<u>Reaction Occurs:</u>	<u>during trapping</u>	<u>with I.R. irradi.</u>	<u>with U.V. irradi.</u>
$(\text{CH}_3)_2\text{SO}$	yes	--	--
H_2S	yes	--	--
Et_2S_2	yes	--	--
OCS	no	no	yes
OCO	no	no	no
SCS	no	no	yes
B_2H_6	no	no	yes
C_3O_2	no	no	yes
$(\text{CH}_3)_2\text{CO}$	no	no	yes

TABLE II

APPROXIMATE GAS-PHASE STRETCHING
FREQUENCIES ($\tilde{\nu}/\text{cm}^{-1}$) OF URANIUM FLUORIDE IONS TOGETHER
WITH MATRIX FREQUENCIES OF NEUTRAL URANIUM FLUORIDE SPECIES

$[\text{UF}_4]^-$	UF_4^*	$[\text{UF}_5]^-$	UF_5^*	$[\text{UF}_6]^-$	UF_6^*	$[\text{UF}_7]^-$
465	532(ν_3)	448	560	520(ν_3)	620(ν_3)	532
480		501	584			553
			647			

* Ref. 2, * Ref. 3 and 4, * Ref. 5

bonds, an increase in ionic character resulting in a decrease in force constant. Moreover, within any given series of alkali metal or alkali metal fluoride reactions, the U-F frequencies of the reaction product usually decrease when descending the Periodic Table, reflecting the decrease in electronegativity of the metal. It is not intended to imply that the strength of the bonds decreases, as the force constant may decrease as a consequence of a broader valley of an ionic potential curve. Decreases in splittings of degenerate bands are also evident as heavier, less polarizing, alkali metals are used. On the basis of their intensity, the bands at 570.8, 548.8, and 526.2 ($^7\text{Li-UF}_6$) and 557.9, 539.2, and 521.9 cm^{-1} (Na-UF_6) are believed to be derived from the T_1 i.r.-active mode of a pure octahedral configuration. These three bands exhibit compression as well as a red shift on progressing from Li to Na. In the M-UF_4 systems, the bands are thought of as being derived from an i.r. active T_2 mode of a tetrahedral configuration, again based on an intensity argument. In this case, however, the separation between the bands does not change appreciably on going from Li to K. This suggests that the metal atom is not responsible for the major splitting; more likely, the extra electron density is perturbing the structure from T_d symmetry and thus the free $[\text{UF}_4]$ ion is not expected to have tetrahedral symmetry.

The observation of an invariant band at 520 cm^{-1} among several M-UF_6 systems is explained as arising from a geometry

in which the metal is separated by several angstroms from the $[\text{UF}_6]^-$ species by argon atoms. This distance is not great enough to prevent reduction of the UF_6 . Electron transfer between separated atoms in molecular beams has been well established for alkali metal-halogen systems whereby the transfer occurs across a separation of 2-3 Å by a process known as "harpooning". It can be pointed out that the electron affinity of UF_6 is $125 \text{ kcal mol}^{-1}$, which is much greater than that of the Cl atom ($87.3 \text{ kcal mol}^{-1}$). A similar type of mechanism to form separated $[\text{UF}_6]^-$ and M^+ is likely. In addition, the ionisation potential of all alkali metal atoms in solid argon is expected to be less than $125 \text{ kcal mol}^{-1}$; thus electron transfer at large distances is energetically allowed. A second electron cannot be added as easily, however, and a contact interaction may be required to form 2M^+ , UF_6^{2-} . Table III presents absorption positions which are expected to be close to free-ion gas phase values for the uranium fluoride anionic species listed. Values were selected on the basis of invariance to metal species and on the assumption that the caesium fluoride- and potassium fluoride uranium fluoride systems will give U-F frequencies closest to free ion gas-phase values. Matrix frequencies are expected to be within 10cm^{-1} of gas phase frequencies, as demonstrated by UF_6 which exhibits a 6cm^{-1} red shift from the gas phase to the matrix for ν_3 .

The assumption of an octahedral $[\text{UF}_6]^-$ anion can be rationalized by a consideration of the orbital energy level diagram of octahedral UF_6 . The lowest-lying unoccupied metal orbital is one of a_u symmetry, for which no Jahn-Teller distortion is expected following occupancy by the one electron from $[\text{UF}_6]^-$. The $[\text{UCl}_6]^{2-}$ anion, also possessing a non-degenerate ground state, has been shown to be essentially octahedral in solution. For this molecule, however, there is a small pseudo-Jahn-Teller effect arising from vibronic coupling of the ground state with a degenerate excited state. This effect is not believed to be significant for analogous fluoro-complexes since the excited states are further removed from the ground state by the higher ligand field strength of F^- . It must be remembered that, according to the Pauling criterion of percentage ionic character, the electron added to UF_6 will not reside exclusively on the metal, but will distribute itself among the six fluorine atoms and uranium to give in this case a negative charge of 0.12 on each fluorine and 0.28 on the uranium.

(b) reactions of lithium atoms with SiF_4

In a typical experiment, lithium metal was vaporized at 435°C and cocondensed with silicon tetrafluoride in an argon matrix for a typical trapping period of 1 h (ar: SiF_4 :100:1). The matrix isolated infrared spectrum showed two bands, located at 853 and 840 cm^{-1} , which could be unequivocally assigned as the ν_3 and ν_1 modes, respectively, of neutral SiF_2 , since the values were identical with those previously reported for the infrared

spectrum of the matrix-isolated molecule in argon. There was some slight band structure between these two peaks which was attributable to either the $(\text{SiF}_2)_2$ dimer or lithium fluoride formed in the lithium atom abstraction process. The absorption band at 598cm^{-1} could be tentatively ascribed to the SiF_2 anion, since this band appeared in the spectrum of the Na^+SiF_2 charge-transfer complex formed in the reaction of sodium metal atoms with silicon difluoride in an argon matrix. It must be emphasized that such an assignment was only tentative, since the other infrared band of the SiF_2 anion was obscured in our spectrum.

The most predominant bands were observed at 1024, 1005, and 1013cm^{-1} and could be attributed to unreacted SiF_4 and matrix splittings associated with this molecule in the argon matrix. The peaks at 990 and 695cm^{-1} could similarly be assigned either to SiF_4 or alternately to Si_2F_6 , Si_3F_8 , or Si_4F_{10} (most likely Si_2F_6), since this band occurs in the infrared spectra of these compounds as an active mode of the terminal- SiF_2 functional group. This same band was also found in the infrared spectrum of $\text{C}_6\text{F}_5\text{SiF}_3$ which is formed in the reaction between silicon difluoride and perfluorobenzene. Assignments attributing these bands to such compounds are reasonable, since their formulation is known to occur when mixtures of SiF_4 and SiF_2 are cocondensed at low temperatures and the mixture is allowed to warm to room temperature. Most certainly, reactions of the type $\text{SiF}_4(\text{s}) + \text{SiF}_2(\text{s}) = \text{Si}_2\text{F}_6(\text{s})$ followed by addition of SiF_2 molecules to form compounds of the

variety $\text{Si}_n\text{F}_{2n+2}$ (Si_2F_6 , Si_3F_8 , etc.) are operative in the $\text{SiF}_2/\text{SiF}_4$ reaction system. An alternate route for the formation of Si_2F_6 would be the dimerization of the trifluorosilyl radical, SiF_3 , produced by lithium abstraction of one of the fluorine atoms from the original SiF_4 . Such a process is unlikely, however, since the Si-F bond is strong, and at no time during this study was any evidence obtained for the existence of the SiF_3 radical which has become previously studied in argon matrices utilizing both infrared and EPR spectroscopy. The total absence of this species in the present experimental system was somewhat surprising in light of the high Si-F bond energy of SiF_4 [$D(\text{Si-F})_{\text{av}} = 142 \pm 2 \text{ kcal}$], but any SiF_2 formed must be reacting to form Si_2F_6 or with further lithium (always kept in excess in these experiments) to form SiF_2^- or SiF_2^- . Furthermore, the infrared spectrum always indicated a decrease in the neutral, molecular SiF_2 with an attendant increase in the perfluorosilanes such as Si_2F_6 or Si_3F_8 when the concentration of SiF_4 was increased in the experiment. Since the infrared data indicated that SiF_2 and SiF_2^- were being formed and isolated in the cocondensation reaction, it was convenient to search for radical species using electron paramagnetic resonance (EPR) spectroscopy, assuming radical recombination does not occur to any significant extent.

The EPR data indicate the presence of a silicon species involving two equivalent fluorine atoms; in addition, the g value suggests that the species is either a radical or a negatively charged molecule. As is the case with the ^{13}C of the methyl

radical, the ^{29}Si is too low in abundance to be observed in the matrix EPR experiment.

The fluorine atom has an unusually large nuclear moment (2.6288 μB) and a previous study on the SiF_3 radical by Merritt and Fessenden, where they reported a hyperfine constant of 136.6 for fluorine, shows that the hyperfine splitting resulting from a fluorine atom can be quite large. Although the hyperfine constant reported here might seem anomalously low in comparison, the magnitude might be appropriate if it is assumed that spin polarization is the cause of the observed hyperfine structure.

On the basis of this analysis, the observed EPR spectrum should be assigned to either the SiF_2 anion or an SiF_2 diradical species. Due to the limitations of both the infrared and electron paramagnetic resonance techniques, unfortunately, the spectra cannot be unequivocally assigned to either chemical form. Because of the relatively low intensity of the EPR lines observed in this reaction, it would appear that this reaction results in no major formation of this radical or anion and surprisingly no trifluorosilyl radicals; alternatively, radical recombination might cause the absence of this radical species.

(c) interaction of CO with metal fluorides

It has been suggested that the shift to a higher stretching frequency observed when carbon monoxide is paired with metal halides or adsorbed on ionic solid surfaces is proportional to

the electric field imposed on the carbon monoxide by the positive metal ion. Co-ordination is assumed to occur through the carbon. It has also been pointed out that the vibrational mode of carbon monoxide is essentially independent of the modes of the metal halide and thus reflects changes which occur only in the carbon monoxide itself.

Previous studies have investigated the effect on the CO stretch of changes in metal ionic radii for metal dihalides. Most of the first-row transition-metal dihalides showed anomalous shifts which were attributed to bonding effects of unfilled d orbitals, whereas calcium, manganese, and zinc difluorides were thought to demonstrate a proportional relation to the positive-ion electric field. We have chosen to study a broad selection of uni-, bi-, and tri-valent metal fluorides in order to evaluate the effect of charge as well as ionic radius.

Table III gives the measured frequency shifts for the $\text{MF}_n\text{-CO}$ pair. Only the highest frequency shift is listed for the alkaline-earth metal difluorides. As indicated by previous workers, a relation does appear to exist between the frequency shift of carbon monoxide and the metal ionic radius. Measured shifts for a particular valence appear to vary as a function of the reciprocal of the square of the metal ionic radius. However, equally good correlations exist for higher orders of the reciprocals of the ionic radius. Thus the importance of any particular type of electrostatic interaction is not suggested. It is also clear that frequency shifts do not vary with formal charge as expected. For

TABLE III
WAVENUMBERS SHIFT (cm⁻¹)

MF_n	$\Delta\nu(CO)$	$\Delta\nu(MF)$	$\gamma(Mn^{n+})^*/A$	Force constant/ mdyn \AA^{-1}	Relative ionic bond character (%)
H	21.0			9.65	44
Li	47.1	27.3	0.68	2.50	100
Na	34.4	11.5	0.97	1.76	100
Mg	67.0	23.3	0.66	3.56	85
Ca	49.3	4.6	0.99	2.43	100
Sr	43.2		1.09	2.15	100
Ba	34.8	3.7	1.21	1.80	100
Cr	50.4	16.6	0.89	3.38	89
Mn	45.2	23.5	0.80	3.87	70
Ni	62.4	65.7	0.69	4.77	83
Cu	72.4	39.3	0.72	4.53	100
Zn	47.9	34.4	0.70	4.68	64
Pb	38.4	10.9	1.03	3.00	83
Sc	74.4	7.5, 9.8	0.732	3.86	89
Y	59.5	6.2	0.893	3.30	97
La	47.2	4.7, 6.3	1.016	2.69	100
Nd	49.4	6.2	0.995	2.93	100
Gd	56.4	5.1, 7.5	0.938	3.13	100
Ho	60.2	5.1, 7.6	0.894	3.32	100
Lu	66.8	4.1, 7.9	0.85	3.51	100
U	46.2	18	0.97		

example, sodium, calcium, and neodymium have approximately the same ionic radius for the uni-, bi-, and tri-valent states respectively. Thus one might expect a simple one to two to three relationship between frequency shifts, but this is not the case. It is possible that a model which considers the presence of fluoride ions and the molecular geometry of the molecular pair might account for these differences.

(d) Chlorination and bromination of UF_4

UF_4 was vaporized at temperatures near 800°C. The matrix gas, argon, was predoped with Cl_2 in Cl_2/Ar ratios of 1/10, 1/50, and 1/100. Br_2 , before being mixed with argon, was subjected to several freeze-thaw cycles under vacuum to remove dissolved gases. All trappings involving bromine were done with a premixed Br_2/Ar ratio of 1/50. Matrix deposition was usually carried out for one hour at 12K trapping temperature. The amount of matrix gas entering the cold surface chamber was kept nearly constant from one experiment to the next by maintaining the back pressure near the matrix gas reservoir at 160 μ . Under these conditions, the pressure in the matrix chamber was about 10^{-5} torr. After initial co-condensation experiments gave no evidence of reaction, subsequent experiments were performed with the aid of a Hanovia photolysis lamp fitted with a broad band mercury source. A Corning #3484 uv filter was employed in one of the experiments to cut out the radiation capable of dissociating Cl_2 .

On the basis of results obtained from the matrix fluorination of UF_4 , in which the mono- and difluoro addition products were identified, one may reasonably expect analogous mono- and dichloro-compounds. Moreover, the possibility for the formation of two dichloro-compounds, cis and trans, has been introduced into the experiment. Cis and trans additions were indistinguishable in the fluorination experiments, since the end products were identical.

Annealing experiments were necessary to assign the observed bands. Features attributable to the monochloro-compound are expected to decrease in intensity upon annealing as the mobility of chlorine atoms increases and more dichloro-species is formed. This was found to be the case for the $UF_4 + Cl_2$ systems studied. Two bands at 569.8 and 593.4 notably decreased in intensity with respect to the other three strong ones at 581.3, 620.6, and 639.2 cm^{-1} . Continued warming eventually eliminated these two features from the spectrum. The three remaining bands displayed coherent behavior, remaining at nearly the same relative intensities throughout annealing. This observation indicates an origin in a common compound.

The three bands at 581.3, 620.6, and 639.2 cm^{-1} which did not decrease upon annealing are assigned to the UCl_2F_4 molecule. Furthermore, the multiplicity precludes an origin in a trans-structure, which would only exhibit one ir active U-F stretching mode. The U-Cl frequencies are expected to lie below 400 cm^{-1} ,

the lower limit of our spectrometer, on the basis of the previously determined UCl_4 frequency ($\nu_3 = 330 \text{ cm}^{-1}$). With the trans- structure eliminated, the only structural possibility remaining for the dichloro- compound has C_{2v} symmetry, for which a maximum of four U-F bands can exist, two A, one B and one B_2 modes. Three modes are actually observed experimentally for the species assigned to the cis- structure, with the unobserved band probably deriving from a less active A_1 mode. No evidence has been found to support the presence of trans- UCl_2F_4 species. Thus, it may be concluded that the cis- species is the more stable of the two possible isomers. It is of interest to note that the analogous dichloro- compounds, cis and trans- WCl_2F_4 , have been prepared and studied. Although both isomers were detected, the cis- form was found to be present in higher concentrations.

The bands at 569.8 and 593.4 cm^{-1} in the $\text{UF}_4 + \text{Cl}_2$ system which shrink and eventually disappear upon annealing are assigned to the monochloro compound, UClF_4 . The relative intensities of these bands resemble those of the UF_5 system, with the lower frequency band of UClF_4 somewhat weaker in intensity than for its UF_5 counterpart.

Substitution of a $1/50 \text{ Br}_2/\text{Ar}$ matrix yielded the third set of bands listed in Table 1 which seems to represent reaction products analogous to those of the $\text{UF}_4 + \text{Cl}_2$ system. Reaction of UF_4 with Br_2 occurs to a much lesser extent, as reflected by

the much lower intensities of the reaction bands relative to those of UF_4 . Features at 578.3, 613.0, and 631.7 cm^{-1} apparently make up the UBr_2F_4 triplet and have similar band spacings to the Cl_2 system. The bromine products are displaced about 6 cm^{-1} to the red, which is understandable in light of the greater electron density on the uranium as a consequence of the lower electronegativity of bromine.

The bands expected for a UBrF_4 molecule are more difficult to assign, owing to the low intensity of some of the features. The absorption at 569.8 cm^{-1} is only tentatively assigned as the second vibration. Doubt arises from the fact that the separation of these two bands does not approximate those observed for UClF_4 .

(a) Reaction of Sn and SnF_2 with C_2H_4

The present report details the results of the matrix isolation infrared study of the reaction of tin and tin (II) fluoride with ethylene with the reaction products being trapped in argon matrices and represents the first evidence for a reaction chemistry involving the Group 4A elements with olefins in the gas phase. Such data should be quite useful in providing initial insight into the use of tin and tin (II) species as catalysts in several industrially important reaction systems in which high-temperature complexes similar to the ones reported here quite likely exist and serve as reactive intermediates or metastable species for such catalytic processes; also, the initial data gathered here serve as the basis for further work relating to the vapor-phase synthesis of Group IVA metal clusters with olefins as well as metal atom/

organic reagent slurries which can serve as active, synthetic reagents themselves.

Matrix isolation experiments in this laboratory have demonstrated the existence of a reaction when tin vapor and ethylene are cocondensed in an argon matrix.

Utilizing a C_2H_4/Ar ratio of 1/100, one observes absorptions for the free ethylene isolated in the argon matrix as well as a series of new bands appearing at 819, 1039, 1043, 3044, and 3063 cm^{-1} which are clearly attributable to a complex formed between tin and ethylene. These bands compare favorably with those observed by Osin and co-workers in similar metal-ethylene reactions trapped in rare-gas matrices, and thus they can be interpreted as resulting from a donor-acceptor complex in which tin is bonded to ethylene via the π system of the olefin.

In addition to these bands, new ones at 851, 732, and 454 cm^{-1} appear. The 851 cm^{-1} peak is a CH_2 -wagging mode with a value very close to that found in the $Cu(C_2H_4)_2$ (862 cm^{-1}) and Zeise's salt (844 cm^{-1})- $K_2[Cl_2Pt(C_2H_4)] \cdot O_2O$ - investigated by Chatt et al. and other workers. The absorption at 732 cm^{-1} is almost identical in value to 730 cm^{-1} reported for Zeise's salt, this band being attributed to the torsional mode ν_4 in the coordinated ethylene.

The relatively intense, low-frequency band at 454 cm^{-1} is particularly noteworthy, and can be tentatively assigned as a

$\nu(\text{Sn}-\text{C}_2\text{H}_4)$ stretching mode involving a cyclic species in which tin may be pictured as approaching the ethylene molecule laterally and forming a three-membered tin-carbon-carbon ring system containing the doubly bonded olefin component which remains intact. Such a complex has been postulated as a logical intermediate in oxidative-addition reactions of tin (II) halides with multiply bonded carbon-carbon systems to form organotin (IV) derivatives, and the tin-carbon stretching frequencies of the final cyclic tin-olefin species in such reactions lie in the $\sim 400\text{-}450\text{cm}^{-1}$ range; also, the metal-carbon frequencies in several metal-olefin complexes lie in the $400\text{-}500\text{cm}^{-1}$ region.

The absence of a noticeably strong $\nu(\text{C}-\text{C})$ stretching mode in the spectrum, an ethylene mode that should be infrared active upon coordination to tin, can be attributed to the low concentration of the complex relative to the whole trapped tin/ethylene mixture and to the inherent weakness of this mode in the complex; indeed, several attempts to increase the concentration of the tin-ethylene complex in the matrix by varying trapping conditions proved unsuccessful. This band most likely lies in one of the two sets of weak multiplets in the $\sim 1520\text{-}1550\text{cm}^{-1}$ region, an assignment that would be in excellent agreement with those of Ozin et. al. One should not forget, however, that the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ modes are highly coupled in both free ethylene and metal-ethylene complexes, with the band in the $1150\text{-}1350\text{cm}^{-1}$ range assigned as the $\delta(\text{CH}_2)$ mode

in various complexes having significant $\nu(\text{C}-\text{C})$ character, even in the weakly perturbed silver-ethylene complex $[\text{Ag}(\text{C}_2\text{H}_4)]^+\text{BF}_4^-$. A distinguishable multiplet with the maximum absorption at 1265 cm^{-1} appears in the spectrum of the tin-ethylene complex shown here. Annealing the matrix produced no noticeable formation of new products.

$\text{SnF}_2/\text{C}_2\text{H}_4$ Reaction. In the spectrum of the matrix isolated products of the reaction between tin (II) fluoride and ethylene, several processes are evident, two of which concern the reaction of the SnF_2 exclusively without interaction with the ethylene. First, the bands at 522 and 580 cm^{-1} indicate the formation of polymerization products of the type $(\text{SnF}_2)_x$ which have been previously reported in matrix isolation studies of tin (II) fluoride. Second, a broad, intense band envelope at $680\text{--}690\text{ cm}^{-1}$ represents the presence of SnF_4 and thus quite evident disproportionation of tin (II) fluoride to the tin (IV) species and elemental tin (which is observed as the residue in the furnace after each set of experiments) during the volatilization of the SnF_2 at 400°C . As a result, many of the new bands present in the spectrum of the $\text{SnF}_2/\text{C}_2\text{H}_4$ reaction--specifically, those at 821 (819 cm^{-1} in the case of the tin system) and 1040 cm^{-1} (1039 and 1043 cm^{-1} with tin)--also appear in the spectrum of the $\text{Sn}/\text{C}_2\text{H}_4$ reaction discussed above. This is also true of the two bands at 994 and 1024 cm^{-1} which appear in the $\text{Sn}/\text{C}_2\text{H}_4$ system when a large excess of tin vapor is reacted with ethylene; consequently,

they may tentatively be attributed to a species of the type $\text{Sn}_x\text{-C}_2\text{H}_4$ in which several tin atoms are clustered around a single ethylene molecule. Presumably, bands which represent coordinated SnF_4 modes in products (if any) between SnF_4 and ethylene are also present in this broad, unresolved absorption region. As with the $\text{Sn/C}_2\text{H}_4$ matrices, annealing failed to change the spectrum.

In addition to the bands above that are assignable to SnF_2 (both monomeric and polymeric) and SnF_4 , one also observes the appearance of two additional bands at 551.5 and 537.5 cm^{-1} , bands which can be assigned as the shifted ν_1 and ν_3 vibrational modes of the bent (C_{2v} point group) SnF_2 molecule complexed to ethylene. Such a complex results from the π electron donation from ethylene to the tin (II) species, thus causing a concomitant red shift in the tin-fluorine stretching frequencies. The red shifts of 41.3 and 33 cm^{-1} for ν_1 and ν_3 respectively, are somewhat larger in magnitude than those reported by Perry et al. for the similar $\text{SnF}_2/\text{C}_6\text{H}_6$ reaction system, with shifts of 29 and 19 cm^{-1} for these same two fundamental vibrational modes.

(3) Reactions of Metal Atoms with Lewis Bases

(a) Metal atoms and water

Our understanding of molecular beam-water reactions, water-induced thin film impurities, and surface-water reactions of the Group IIIA metals depends in part on our knowledge of the reactivity and reaction paths of atomic and small metal clusters of the Group IIIA metals with water. The matrix isolation technique

along with in situ photolysis affords the opportunity of following the reaction of an atom, diatom, etc., with water from initial interaction, through intermediate products to the final products.

Calculations and experiments suggest that when water bonds to Li, Na, and Al through the oxygen an adduct of C_{2v} symmetry is formed. Calculations have also shown that the metal becomes slightly negative in the adduct owing to a small amount of electron donation from water to the metal as might be expected in a Lewis acid-base type interaction. The sensitivity of the ν_2 bending mode of water to adduct formation may be understood by reference to the photoionization spectra of water which indicate that ionization from the $1b_1$ orbital causes small decreases in both the bending ($\Delta\nu = -225\text{cm}^{-1}$) and stretching ($\Delta\nu = -437\text{cm}^{-1}$) frequency of water along with a bond-angle increase of $\sim 5^\circ$. Ionization from the $2a_1$ orbital results in a large decrease in the bending mode ($\Delta\nu = -687\text{cm}^{-1}$) and no observable change in the stretching mode, as well as a bond-angle increase to 180° . The ν_2 bending mode and bond angle of water are clearly much more sensitive to electron loss from the $2a_1$ (σ lone pair) orbital of water than the $1b_1$ (π lone pair) orbital. As mentioned by Potts and Price, the $2a_1$ orbital in a linear AH_2 molecule is nonbonding and in a bent molecule acts primarily as a shield to the mutual repulsion of the two hydrogen nuclei. Thus, one expects electron density loss in the region between the hydrogens to lead to a larger angle

and lower frequency. Little effect would be expected on the oxygen-hydrogen bonds because of the largely nonbonding character of the $2a_1$ orbital with respect to these bonds. Consequently, electron donation from the $2a_1$ orbital of water into the partially or unoccupied a_1 orbitals of the metal should be marked by a decrease of the bending mode frequency but little or no change in the stretching modes.

The $1b_1$ orbital is also nonbonding in a linear AH_2 molecule but does not provide significant stabilization of the bent molecules as does the $2a_1$ orbital. As a result, electron donation from the water $1b_1$ orbital into a b_1 orbital of the metal should not affect the bending frequency of water.

Thus changes in ν_2 should primarily reflect perturbation or σ bonding to the metal of the $2a_1$ orbital of water. Our general observations indicate a decrease in the bending mode of water and no observable shift in the stretching modes of water upon formation of a metal-water adduct.

A comparison of the shifts in the ν_2 -water bending mode for water adducts of the alkali metals Na (-7.4cm^{-1}), K (-6.6cm^{-1}), and Cs (-2.7cm^{-1}) to the Group IIIA metal of the same row indicates a factor of 3 increase in $\Delta\nu_2$ for the Group IIIA metals. This suggests that the corresponding Group IIIA metal interacts much more strongly with a water molecule than the respective alkali metal atom. Since aluminum reacted spontaneously, a measured $\Delta\nu$ was not obtained but one can estimate a value of -24cm^{-1} by comparison to $\text{Na}\cdots\text{OH}_2$. Assuming a general linear relationship

between $\Delta\tilde{\nu}$ and interaction energy, one predicts an interaction energy of ~16 kcal for $\text{Al}\cdots\text{OH}_2$ by comparison to Li (17.5 cm^{-1} , 11.7 kcal). This may be compared to values of 4.4 and 8.5 kcal from calculations of Trenary and Kurtz, respectively. The lack of agreement between the calculated and estimated value suggests that the correlation between $\Delta\tilde{\nu}$ and interaction energy is not a general one and that it may work only within a specific group. This is not surprising if the bending frequency is reflecting only a σ donation of the water and not π bonding of the $1b_1$ orbital or back-bonding from the metal into the unoccupied $2b_2$ antibonding orbital of water.

Although the quantitative relationship of $\Delta\tilde{\nu}$ to interaction energies is unclear, it seems likely that the interaction energies should follow in some manner the $\Delta\tilde{\nu}_2$ change. Thus it appears that the diatomic Group IIIA molecules are more weakly bonded to water than is the atom. One expects Ga, In, and Tl atoms to bond in a similar manner to aluminum atoms, however, the type of interaction between diatomic species and water is not obvious since it may either exist as an interaction with a single metal atom or as a bridging interaction with bond atoms.

The photoinduced reactivity of the Group IIIA metal-water adduct with respect to formation of the divalent metal hydroxyhydride is seen to vary from spontaneous reaction of aluminum to no reaction for thallium. It is interesting that the inability to form HTlOH agrees with the ΔH estimate given in Table I which indicates that HTlOH is unstable with respect to $\text{Tl}\cdots\text{OH}_2$.

The HMOH molecule is expected to have C_5 symmetry owing to the presence of the one unpaired electron which should result in an HMO bond angle of less than 180° . The number of infrared-active modes would be six with the two lowest modes being MOH bond angle deformations both in and out of the molecular plane. The trend of assigned HMO bending mode with respect to atomic number exhibits unusual behavior in that the aluminum HALO bending mode is less than that for gallium and indium. This may be due to a decreased HMO bond angle for the heavier Group IIIA atoms as is the case for the Group IVA metal dihalides.

This behavior is also evident in the assigned MOH bending mode for HGaOH. A similar mode was not observed for HALOH under conditions where the other modes of HALOH were quite strong. Thus it seems likely that its value is less than that for gallium and less than 400 cm^{-1} .

It was mentioned earlier that the deuterium stretching mode of DALOD was much weaker and broader than expected. This is thought to result from a Fermi interaction of the D-Al stretching mode with a combination of the DALO bending and Al-OD stretching modes.

The isotopic shifts, in general, confirm the assignment of observed frequencies to particular modes. However, one notes that the M-OH mode undergoes rather strange shifts upon deuterium substitution. This is particularly evident for indium, where deuterium substitution causes an increase in the M-OH mode. This behavior can be explained if one assumes molecule C_∞ symmetry.

With this molecular symmetry the three lowest observed modes are expected to undergo partial coupling to each other. Deuteration will cause changes in the extent of coupling between the modes which, in turn, leads to the unusual isotopic shifts. This coupling would not occur for a linear molecule with $C_{\infty v}$ symmetry. Thus its existence is further evidence for a nonlinear molecule.

A similar effect exists for the MOH molecules. This is evident for a comparison between calculated and measured isotopic shifts of the M-OH mode where the shifts have been calculated for a linear geometry and assumption of the absence of any coupling between the OH and M-OH stretching modes. The calculated shifts are compared to measured values in Table III. One sees an increasing discrepancy between the calculated and measured values with increasing mass of the Group IIIA metal. These discrepancies can be explained by changing coupling of the MOH stretching and bending modes of a nonlinear molecule.

The photolytic reaction of diatomic Group IIIA molecules with water occurs at longer wavelengths than for the atom and produces a group of absorption peaks in the $850\text{--}1050\text{cm}^{-1}$ region. Deuterium isotopic shifts indicate that the vibrational mode is primarily a hydrogen motion, although there is a slight oxygen-18 dependence. We have suggested that the mode may be best explained as an asymmetric mode of a bridging hydrogen. The location of modes due to a bridging hydrogen should be ~ 1000 and $\sim 900\text{ cm}^{-1}$ for gallium and indium, respectively, if one assumes a similar ratio

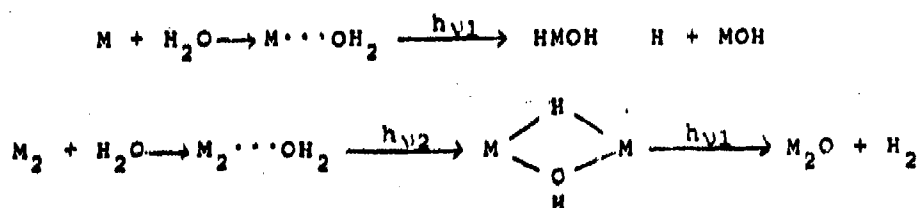
of frequencies as that found for the asymmetric bridging and terminal stretching modes of diborane. One also expects the hydroxyl group to be bridging. It is possible to view the HM_2OH molecule as a mixed dimer of monovalent MH and MOH species which suggests that dimers of MH and MOH would also exist as bridging structures. Prolonged photolysis at shorter wavelengths converts the HM_2OH species to the known high-temperature M_2O species.

The dihydroxyaluminum hydride has been identified and presumably results from further reaction of the $\text{HAlOH}(\text{H}_2\text{O})$ species. We did not observe a similar dihydroxy species for gallium and indium, which may suggest that the higher oxidation state $\text{HM}(\text{OH})_2$ is unstable with respect to the $\text{MOH}(\text{H}_2\text{O})$ species. In fact, the unassigned peaks listed in Table III for indium could be due to $\text{InOH}(\text{H}_2\text{O})$.

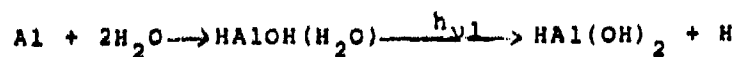
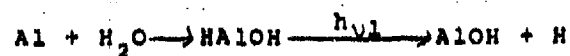
The inability of thallium to react was discussed earlier. However, after prolonged photolysis, we do observe a peak labeled "h". We have suggested that the peak may be assigned to TlOH or $\text{TlOH}(\text{H}_2\text{O})$. Although the reaction is endothermic and the excited state HTl^*OH is expected to revert to $\text{Tl}\cdots\text{OH}_2$, some probability may exist for breaking of the H-Tl bond and subsequent diffusion of the hydrogen into the matrix, thereby stabilizing the TlOH species. The alternative assignment as $\text{TlOH}(\text{H}_2\text{O})$ formation could result from stabilization of TlOH by

interaction with water. It is interesting to note that a dihalium product species does readily form, which suggests that a bridging structure has stabilized the hydrogen and hydroxyl bonds sufficiently to favor the photolysis product over the adduct.

The reaction chemistry of Group IIIA metals with water may be summarized as follows:



The exception is Al, which spontaneously reacts with water as follows:



(b) metal atoms and methane

The activation of inert bonds with transition metals has been recognized as an important goal. We report some of our results on the reactions of photoexcited metal atoms with methane.

Our work indicates that no reaction occurs between iron

atoms and methane at 15K. Irradiation with $\lambda = 360$ nm causes a new set of peaks at 1653.4, 1153.4, 548.8, 545.9, and 521.1 cm^{-1} to appear. The isotopic shifts observed indicate that the 521.1- and 1653.1 cm^{-1} peaks can be assigned to the iron-carbon and iron-hydrogen stretching modes, respectively, and suggest that oxidative cleavage of a carbon-hydrogen bond has occurred to yield CH_3FeH . The other peaks can be assigned to the hydrogen modes of the methyl group.

Wavelength-dependent photolysis studies indicate that reaction is caused by absorption of the metal atom rather than the metal dimer. Thus, the iron-methane matrix was first irradiated with light which could only photoexcite the assigned electronic transition of the metal dimer; however, the photo-induced reaction was observed only when light was present in the region where the free metal atom is known to absorb.

Similar results were obtained when other metals were codeposited with methane and irradiated. Thus, Mn, Co, Cu, Zn, Ag, and Au all reacted with methane to give insertion products analogous to CH_3FeH , whereas Ca, Ti, Cr, and Ni failed to yield insertion products. The infrared absorption frequencies of these products are presented in Table IV.

TABLE IV
Product Band Positions (cm^{-1}) in
Photoexcited Metal Atom/Methane Reactions

metal atom	band positions, cm^{-1}			
	$\nu_{\text{C-H}}$	$\nu_{\text{M-H}}$	ν_{CH_3}	$\nu_{\text{M-C}}$
manganese	2932.9	1582.6	1142.3	550.3 546.2
iron	2933.5 2908.6	1653.1	1153.4	548.8 545.9
cobalt		1699.5		585.4 576.7
copper		1855.7	1200.1	613.8 433.9 417.4
zinc		1845.8	1069.5	689.1 447.1
silver	2907.6 2900.1	1725.8	1232.4	614.7
gold		2195.8	1202.8	610.9

(4) Synthesis of Metal Oxyfluorides

Preparation of the oxyfluorides of scandium, lanthanum, cerium, yttrium, and aluminum were attempted. For La, Y and Al, a stoichiometric mixture of the fluoride and oxide of the metal was reacted in an evacuated quartz tube at 1000C according to the formula: $MF_3 + M_2O_3 \rightarrow MOF$. Comparison with published x-ray powder diffraction data (Zachariasen 1951) suggests the formation of LaOF and YOF as predominant products of their respective reactions, although quantitative analyses of LaOF by Galbraith Laboratories indicate a deficient fluorine content. AlOF failed to form as a crystalline material.

(5) Synthesis of Metal Nitrifluorides

Direct fluorination of metal nitrides should yield metal fluorides + N_2 , and there is no literature evidence for ternary M-N-F species. These experiments verify the literature reports.

Lanthanum nitride--a coating was formed on the outside of the nitride particles; evidently the product is unreactive towards moist air (LaN reacts immediately in moist air to give La_2O_3). X-ray analysis showed however no La-N-F lines and only LaN and LaF_3 . At low temperature of fluorination the above reaction occurs and at higher temperatures (600C) complete fluorination to LaF_3 occurs. Covalent fluorides Si_3N_4 and BN do not fluorinate at moderate temperatures. No reaction was observed for LaB_6 and F_2 .

REACTIONS OF METAL FLUORIDES WITH METAL NITRIDES

$\text{LaN} + \text{LaF}_3$ --powder obtained gave good x-ray pattern agreement with published values. No sintering was achieved and no large single crystal was formed (900C).

$\text{CeN} + \text{CeF}_3$ --(CeN prepared in lab)--no Ce-N-F product obtained (900C)

$\text{HfN} + \text{HfF}_4$ --some very faint product lines, not HfN or Hf_4 ; predominant lines were reactant (1000C)

$\text{TiF}_3 + \text{TiN}$ --no product obtained (1000C)

$\text{TaF}_5 + \text{TaN}$ --no product (3 explosions!) (600C)

$\text{YF}_3 + \text{YN}$ --no product (400-900C)

$\text{Fe}_2\text{N} + \text{FeF}_2$ --no product (300C)

$\text{Cu}_3\text{N} + \text{CuF}_2$ --no product (900C)

$\text{AlF}_3 + \text{AlN}$ --some product not reactants--elemental analysis was inconclusive. X-ray lines not assigned--could possibly be reaction with quartz vessel (900C).

REACTIONS OF METAL FLUORIDES WITH AMMONIA

$\text{AlF}_3 + \text{NH}_3$ --product formed (strong lines not reactants).

Mass spec. shows fluoride species and also NF_3^+ (possibly) no molecular ion present to 1100C. Also some unusual peaks not identified.

50 psi NH_3 in static reactor to 900C.

$\text{ZrF}_4 + \text{NH}_3$ --colored product (from white ZrF_4). X-ray shows ZrN & ZrF_4 ; 500C 30 psi.

$\text{TiF}_3 + \text{NH}_3$ --bluish-gray product from TiF_3 ; no reaction (TiF_3 lines only in x-ray); 750C, 50 psi.

$\text{LaF}_3 + \text{NH}_3$ --excellent product & good agreement with published data; 50 psi, 900C. No sintering possible to 1000C.

$\text{CeF}_3 + \text{NH}_3$ --no reaction, 500C, 50 psi.

$\text{FeF}_2 + \text{NH}_3$ --no reaction, 500C, 50 psi.

$\text{FeF}_2 + \text{NH}_3$ --reduction to Fe metal 900C, 50 psi.

$\text{NiF}_2 + \text{NH}_3$ --reduction to Ni metal 900C, 50 psi.

$\text{YF}_3 + \text{NH}_3$ --YN + YF_3 , no ternary product observed--900C, 50 psi.

$\text{CuF}_2 + \text{NH}_3$ --no reaction, 500C, 50 psi.

(6) Further Studies of CFX

We have published an extended review of the properties of CFX in Accounts of Chemical Research and continue to seek alternate synthetic materials which would not require elemental fluorine. Thus, a weakly bonded fluoride like ZrF_2 or HgF_2 could be caused to treat a hydrocarbon, activated carbon or pyrographite and form the solid fluorocarbon.

Also, we are attempting to develop reliable analytical methods for establishing the CF_{1+x} stoichiometry with precision and accuracy. Newton atomization studies have given erratic results, apparently dependent on sample density, geometry and reference materials. Thermal decomposition in vacuum or inert atmospheres (A_2 or N_2) yields an amorphous carbon + CF_4 . This method appears to be the best current analytical technique.

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8/1/78-12/31/80

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